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Biological Treatment of Aqueous Hazardous Wastes

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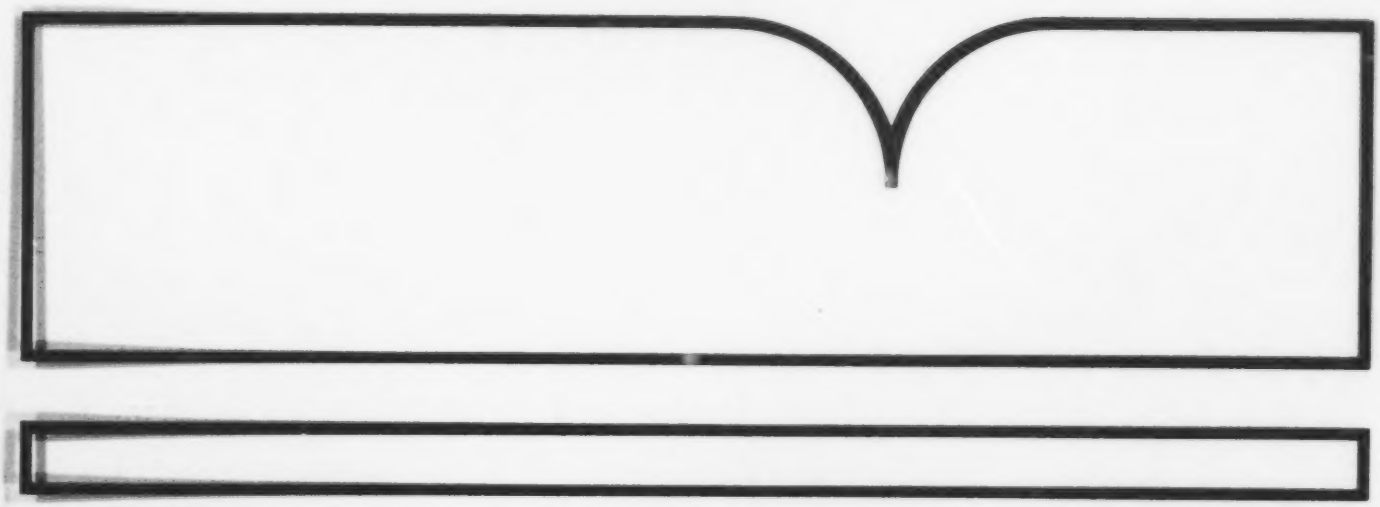

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BIOLOGICAL TREATMENT OF AQUEOUS HAZARDOUS WASTES

by

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16. ABSTRACT

This paper describes tests performed in order to evaluate the fate of aqueous organic hazardous waste compounds in the activated sludge process. Gas, liquid and waste solids samples were taken from acclimated activated sludge systems to determine amounts that were volatilized, biodegraded and associated with the wasted solids. Results discussed here include two compounds, methyl ethyl ketone and 1,1,1-trichloroethane.

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Biological Treatment of Aqueous Hazardous Wastes

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This paper describes tests performed for the purpose of determining the fate of components of aqueous organic hazardous waste streams when treated in an activated sludge process. Liquids, waste solids, and gas samples were taken from acclimated bench-scale systems to establish the amounts that were biodegraded, volatilized or sorbed on the wasted solids. The results discussed here include two compounds, methyl ethyl ketone and 1,1,1-trichloroethane.

Introduction

As a result of the reauthorization of RCRA and the concurrent restrictions on land disposal of hazardous wastes, the USEPA is assessing waste treatment techniques that can be substitues for, or precursors to, land disposal. Concentrations of hazardous, organic compounds in aqueous, RCRA-listed wastes must be greatly reduced in order to reach levels acceptable for land disposal. The environmental consequences of utilizing treatment techniques to meet these limitations must be determined.

Large volumes of aqueous, hazardous wastes are produced which have concentrations of organics between 1 and 10,000 ppm. Wastewaters with organic concentrations within this range will generally be too low for efficient recovery of organics via physical separation, and may be too high for discharge. Biological treatment, specifically, activated sludge, can significantly reduce the concentrations of many hazardous organics present in such wastewaters and has been designated the Best Demonstrated Available Technology (BDAT) for treating such waste streams. Considering the toxicities and the high concentrations of many of the compounds present in hazardous waste streams, it becomes critical to know the fate of each compound: volatilization or stripping may present a health problem for treatment plant operators, high concentrations in the sludges may preclude land disposal, and recalcitrance may indicate the need for a different treatment approach.

The fate of toxic organics in the activated sludge process has been well-studied by both industry and academia. Kincannon and Stover, et. al. (1981, 1982, 1983) have studied the treatability and fate of many priority pollutants at concentrations above 100 mg/l. Freeman, et. al. (1982, 1984) have investigated the theoretical stripping of organics as well as treating the strippability of acrylonitrile.

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Blackburn, et. al. (1985a & b) have described a series of experiments aimed at developing predictive fate models. Kirsch, et. al. (1986) have described a protocol for developing such predictive models.

The purpose of this work was to establish the fates of the organic components of hazardous waste streams in well-run activated sludge systems. Two important aspects of this testing program were to determine how the fates of selected compounds change with concentration, and to be able to determine the fates of the components of real world hazardous wastes. The first can be accomplished by successively acclimating a system to three concentration levels, up to the specific compound's solubility limit. As this paper was being prepared, results had been obtained for two compounds at the first of three planned concentration levels for each. The second aspect, the testing of actual hazardous wastes, will be the focus of work to follow in the near future.

Materials and Methods

To date, two complete systems have been set up and operated. Each test apparatus consisted of a completely-mixed, continous flow, glass reactor (6" I.D. cylinder) and two glass clarifiers (primary and secondary). The liquid volumes of the reactors were 11 liters, while the clarifiers had liquid volumes of 1.5 liters. A flow rate of 11 liters per day was used for both systems, resulting in 24 hour hydraulic retention times (HRT), which although long, are consistent with those used by some industries, for example, the 26 hour HRT reported by Campbell and Rocheleau (1976). The reactors were air-mixed using air-stone diffusers. All vessels were closed: off-gases passed through air sampling/ventilation tubing. Settled sludge was returned to the reactor via a recycle pump on a timer. A peristaltic pump was used to provide the influent flow. The test compound was introduced through a syringe pump. The spike was mixed with the influent as it flowed through a series of small-diameter mixing loops before entering the primary clarifier. Ten percent of the reactor volume was wasted directly from the reactor on a semi-continuous basis using a peristaltic pump operating intermittently (23 ml every 30 minutes). The wasting rates for both systems were set to produce theoretical SRT's of 10 days. Waste sludges were pumped to a holding vessel in the refrigerator. Influent and effluent samples to be analyzed for the test compound were continually pumped at low flow rates (0.7 ml/min) into teflon bags in the refrigerator. Grab samples of primary effluent were taken. All liquid and solids samples were carefully transferred to clean amber glass bottles which were sealed without headspace. Primary, secondary, and reactor off-gases were sampled using 0.63 cm O.D. borosilicate glass traps packed with 0.25 g of Tenax. Two traps were used in series for each sample. Air sampling pumps were used to supply the appropriate rate of air flow (50 ml/min), which was further controlled by needle valves and measured by rotameters. A flow of air was maintained through the clarifiers at all times. A half hour prior to off-gas sampling,

purified air, at atmospheric pressure was supplied to each clarifier. Teflon tubing and connectors were used for off-gas sampling and for liquid delivery and sampling

A synthetic feed, as described by Kincannon (1983), was prepared daily and stored in a refrigerator at 4°C. The SBOD of the feed was approximately 500 mg/l; the average SOC was approximately 420 mg/l. A synthetic feed was chosen to facilitate comparisons between test runs with different compounds as well as to ensure a stable source of substrate and nutrients. The initial activated sludge seed was a return activated sludge from a larger system operated at the Test and Evaluation Facility (T&E). Both test units were acclimated to the feed for at least one month prior to initiation of spiking. During this period, the mixed liquor volatile suspended solids ranged from 800 to 1100 mg/l. The effluents of both systems were usually below 30 mg/l BOD and 30 mg/l VSS.

The routine process monitoring measurements and their respective frequencies are shown in Table 1.

Table 1. Routine Process Monitoring

Measurement	Frequency	Method
$SBOD_5$	3x per week	EPA 405.1
SOC	5x per week	EPA 415.2
TSS/VSS	1x per day	EPA 160.1
D.O.	6x per day	EPA 360.1
D.O. uptake rate	1x per day	St. Meth. 213A

The air provided to the reactors was based on the six daily dissolved oxygen readings. The goal was to keep the D.O. between 2.0 and 6.0 mg/l. The lower limit for air flow that provided adequate mixing was found to be about 0.8 liters/min. All air flow readings during the first test concentrations for both systems were between 0.8 and 1.0 liters/min.

Following acclimation to the base synthetic feed, the specific test compound was introduced. Both systems were allowed to acclimate to the first concentration for a period of at least one month. The test phases were begun when the daily MLVSS values had been relatively steady, and the soluble effluent TOC and BOD values had indicated good effluent quality (both SOC and SBOD < 30 mg/l). The sampling program for the test compounds consisted of 24-hour composite liquid influent and effluent samples, a 24-hour composite mixed liquor sample, a grab primary effluent sample, and three grab off-gas samples. This program was repeated three times per week for a minimum of six sample sets. Gas chromatographic analyses followed EPA-approved methods. (EPA, 1984).

Results

The results presented here are those of the first of three concentrations for methyl ethyl ketone (MEK) and 1,1,1-trichloroethane (TCA). These two compounds were chosen from a list of solvents for which activated sludge had been tentively deemed BDAT (Federal Register/ Vol. 51, No. 9, Jan. 14, 1986). Testing TCA also permitted comparison with the results of existing data, verifying the system's overall performance. The goal of this study was to test three concentrations, evenly spaced within the range of each compound's solubility in water. Since much of the existing fate data is comprised of compounds at concentrations up to 100 mg/l (e.g. Kincannon, et.al., 1983), it was decided that this concentration range would be an appropriate starting point. The first concentrations tested were: 55 ± 9 mg/l for MEK and 141 ± 37 mg/l for TCA. The second concentrations will be approximately 500 mg/l for both MEK and TCA. The concentrations tested will be an order of magnitude higher than the second, provided inhibition, toxicity or insolubility are not encountered.

Two important considerations of this testing program were that the systems were well operated, and that sampling would take place while they were in a nominally steady-state condition. A well operated system was defined as a system that produced a good quality effluent. Steady-state was defined in terms of consistant mixed liquor volatile suspended solids. The performance data for both systems is shown in Table 2. All values are 14-day means, shown with their standard deviations. The most questionable parameter relative to the preceeding discussion was the effluent volatile suspended solids (VSS). The high effluent VSS values indicate upsets to the systems caused by the introduction of the test compounds. Bridging of the sludge solids in the conical bottom of the secondary clarifier was observed. This may have prevented adequate return of solids to the reactor. In both systems the VSS removals had increased with time, indicating that they were approaching a steady state. Despite the high levels of VSS in the effluents of both systems in their respective preceeding two week periods (lowering the SRT), in both cases, it was decided to proceed with sampling. It was felt that the SOC and SBOD data had been very consistent, and that a steady state condition was imminent. As can be ascertained from the performance data, absolute steady states were not achieved in either case. This was mitigated somewhat by the number of sample sets (seven) and by the fairly consistent MLVSS concentrations.

The specific fates determined were: volatilization in the primary, stripping in the reactor, sorption onto or association with, the biomass, secondary volatilization, secondary effluent, and biodegradation. All of these except biodegradation can be directly measured by sampling the off-gases, liquid effluents and the waste sludge. The concept of "association with the biomass" is an artifact of the analytical method (purge and trap) used for the two compounds tested. Any attempt to extract these two compounds from the biomass and theoretically measure sorption would undoubtedly result in volatilization and produce an inaccurate measurement. The method used for these experiments measures the amount of the compound that remained with the waste sludge, after it

Table 2. Process Monitoring Data

(all values in mg/l)

	MEK Before†/During Testing		1,1,1 TCA Before*/During Testing	
MLVSS	779 ± 121	1093 ± 336	958 ± 129	1335 ± 178
Effl. SBOD	---	18 ± 6	17 ± 16	63 ± 53
Effl. SOC	38 ± 21	16 ± 8	20 ± 12	27 ± 14
Effl. VSS	101 ± 62	44 ± 22	134 ± 112	91 ± 65

*For a two week period prior to testing
†For a two week period prior to last five sample days

had been exposed to the stripping potential present in the reactor. The amount biodegraded was found by performing a mass balance: the amount volatilized or stripped, the amount in the effluent and the amount associated with the biomass were subtracted from the reactor input (primary effluent). An important assumption was that all reactions, (photolysis, hydrolysis, and bio-oxidation) were lumped into what may be termed "apparent biodegradation".

For the first concentration level of each test compound, samples were collected on seven days. The mass fluxes and the mean percentages of the influent mass distributed to each fate as calculated from a mass balance around the primary clarifier and a mass balance around the reactor/secondary clarifier are shown in Table 3.

In addition to the mass balance calculation for biodegradation, mass balances around the primary clarifiers were also calculated. The difference between the influent flux and the volatilization plus the primary clarifier effluent fluxes is reported in Table 3 as an unknown loss or gain. This difference is most likely due to variance in sampling and/or analysis. TCA is heavier than water and may have partially stratified in the primary clarifier. This may also account for part of the apparent TCA loss. The apparent gain in MEK may be due to the difference in sample collection techniques between the influent (24-hr composite) and the primary effluent (grab). It is possible that a small amount of additional biodegradation of the MEK occurred, even at 4°C, over the composite period.

Discussing the compounds individually, greater than 94% of the influent MEK was shown to be biodegraded. In a better-operating system, even more biodegradation would be expected. MEK was not found above the detection limit in the effluent. A detection limit of 0.10 mg/L was used for the mass balance calculations. An interesting finding was

Table 3. Fates of MEK and TCA in Activated Sludge

	MEK		TCA	
	Flux (mg/min)	%	Flux (mg/min)	%
	PRIMARY MASS BALANCE			
Influent	0.418		1.072	
Primary Effluent	0.404	96.66	0.741	69.0
Primary Volatilization	0.046	11.00	0.221	20.6
Unknown Prim. Loss (+)/Gain(-)	-0.030	-7.66	0.110	10.4
	SECONDARY MASS BALANCE			
Biodegradation	0.382	94.55	0.161	21.77
Reactor Stripping	0.012	3.04	0.565	76.22
Secondary Volatilization	0.0002	0.05	0.004	0.52
Waste Sludge	0.0004	0.10	0.001	0.14
Effluent	0.009	2.26	0.010	1.35

that more MEK volatilized under quiescent conditions in the primary clarifier than was stripped from the reactor. This would tend to support the notion that MEK is very easily biodegraded.

The TCA results can be compared to those of Kincannon, et. al. (1983). They found that with an influent of 118 mg/l TCA, stripping accounted for 100% of the removal, with 1.6 mg/l remaining in the effluent. The average TCA concentration in our effluent samples was 1.3 mg/l, and stripping accounted for approximately 76% of the removal from the reactor. TCA can be biodegraded, as shown by Tabak et. al. (1981). Given this test system's extended acclimation period, (one month at 10 mg/l, three months at 141 mg/l), the 21% apparent biodegradation of TCA is not unreasonable. As was true for MEK, a significant portion was volatilized in the primary clarifier.

These are the preliminary results of a continuing testing program. As the work proceeds, it will be possible to determine how the relative fates of these compounds change with concentration. Future work will also include determination of the fates of the multiple-component mixes which make up actual hazardous wastes.

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